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■ CO₂-fluxing collapses metal mobility in magmatic vapour

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Abstract

Magmatic systems host many types of ore deposits, including world-class deposits of copper and gold. Magmas are commonly an important source of metals and ore-forming fluids in these systems. In many magmatic-hydrothermal systems, low-density aqueous fluids, or vapours, are significant metal carriers. Such vapours are water-dominated shallowly, but fluxing of CO₂-rich vapour exsolved from deeper magma is now recognised as ubiquitous during open-system magma degassing. Here, we show that such CO₂-fluxing leads to a sharp drop in element solubility, up to a factor of 10,000 for Cu, and thereby provides a highly efficient, but as yet unrecognised mechanism for metal deposition.

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Introduction

Aqueous vapour is increasingly recognised as an important agent of element mobility in the crust (Hedenquist and Lowenstern, 1994; Pokrovski *et al.*, 2005; Williams-Jones and Heinrich, 2005; Migdisov *et al.*, 2013). Vapour is particularly common in magmatic environments, and can be sampled directly at fumaroles and volcanic plumes. Compared to the source magma, vapours can be strongly enriched in metals (*e.g.*, Allard *et al.*, 2000; Williams-Jones and Heinrich, 2005; van Hinsberg *et al.*, 2016), and metal mobility in shallow magmatic conduits is well-established (*e.g.*, Berlo *et al.*, 2013; Plail *et al.*, 2014). Although evidence for high metal solubility in vapour inclusions in rocks is debated (Lerchbaumer and Audétat, 2012), experiments reproduce these high solubilities (Migdisov and Williams-Jones, 2013; Migdisov *et al.*, 2013), thereby conclusively confirming that vapours are capable of transporting metals in high concentrations.

The ligands available to elements in aqueous vapour and liquid are similar, although charged species are unimportant in vapour and, instead, uncharged molecules dominate element transport. However, the concentrations of metals in vapour inferred from fumarole emissions and fluid inclusions are commonly orders of magnitude higher than is predicted from metal volatility. The reason for this is the ability of water molecules to form hydrogen-bonded clusters that incorporate metal-bearing molecules, thereby significantly increasing stability, and hence solubility of the latter in the vapour phase. Recent experiments (Migdisov and Williams-Jones, 2013; Migdisov *et al.*, 2013; Hurtig and Williams-Jones, 2014) have demonstrated this effect for Cu, Ag and Au, and show that the complexity of these hydration clusters, and with them the stability of metal-bearing clusters, increases exponentially with increasing water vapour pressure. At the highest densities, the vapour can no longer be considered a low-density fluid as the previously isolated water clusters merge into the 3D hydrogen-bonded network typical of dense aqueous solutions.

The density-, or pressure-dependence of metal solubility has been used to explain metal deposition during earthquake-induced depressurisation (Weatherley and Henley, 2013) and fluid ascent in volcanic-hydrothermal systems (Henley and Berger, 2013). Depressurisation, however, is not the only mechanism that destabilises these clusters. Reducing the *partial* pressure of water, *i.e.* changing the vapour's composition, produces the same effect. For example, dilution of water-rich vapour with a non-polar gas such as CO₂, results in a drop in the partial pressure of water (*p*H₂O), and hence destabilisation of hydrated metal-bearing clusters, comparable to that occurring during depressurisation. This effect is entirely independent of the total pressure or density of the system, and can be large even when the density (or *P*_{total}) of the mixed fluid rises during this dilution.

In the following, we will show that fluxing of CO₂-dominated vapour, released during degassing of deep-seated magma and known to transit magmatic-hydrothermal conduits, reduces *p*H₂O significantly, leading to near-total collapse of the metal transporting capacity of the vapour.

CO₂-Fluxing in Magmatic Conduits

The solubility of volatiles in magma is controlled dominantly by pressure (Dixon *et al.*, 1995; Spilliaert *et al.*, 2006a) as are, therefore, the resulting exsolved fluid compositions. CO₂ is the first major volatile to exsolve, and deep-released magmatic fluids are CO₂-dominated, with H₂O becoming more important as pressure decreases, followed by S, Cl, and F (Spilliaert *et al.*, 2006a).

Magma ponds and exsolves volatiles at different levels in the crust, and can experience stages of closed- and open-system degassing. These volatiles are buoyant and flux through the overlying magmatic conduit, intermediate ponding levels, and the system's host rocks. Fluxing of CO₂-rich gas through shallower

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magma results in CO₂ enrichment and melt dehydration (Spilliaert *et al.*, 2006b). High CO₂, low H₂O melt inclusions are now widely recognised, and generally attributed to CO₂-fluxing (Spilliaert *et al.*, 2006b; Blundy *et al.*, 2010). Gas fluxing has also been linked to enrichments in Cl, alkalis, Ti, Fe, and P (*e.g.*, Ferlito *et al.*, 2007), Cu (Collins *et al.*, 2009), and Li (*e.g.*, Berlo *et al.*, 2004). These element enrichments are generally interpreted in terms of repressurisation, fluid boiling or crystallisation, but we argue here that changes in metal-complex stability resulting from CO₂-fluxing are an attractive alternative.

The pressure dependence of volatile-element solubility in magma leads to sharply different compositions of the exsolved fluid at different depths. A fluid in equilibrium with a typical MOR basalt at 1300 °C will contain 83 mole % CO₂ and 4 % H₂O at 1000 bar, but 17 mole % CO₂ and 61 % H₂O at the surface (Gaillard *et al.*, 2012). To evaluate the impact of such drastic changes in composition, in particular in pH₂O, on the ability of magmatic vapour to carry metals, and the potential of CO₂-fluxing as a metal deposition mechanism, we modelled a vapour-filled fracture network in a magmatic-hydrothermal system subjected to a pulse of CO₂-rich vapour (Fig. 1). Given that our purpose is to highlight the effects of CO₂, we will explore endmember scenarios, rather than a specific geological case.

Impact of CO₂-Fluxing on Metal Solubility

In the simplest scenario, a CO₂-rich vapour pulse, released from mafic magma at 1000 bar, passes through shallower, water-dominated vapour at 800 °C. To model this, we used gas compositions in equilibrium with mafic magma at various depths (Gaillard *et al.*, 2012) at constant pHCl = 0.005 (Migdisov *et al.*, 2013), a Cu content buffered by chalcopyrite-pyrite coexistence (thermodynamic data sources as in Migdisov *et al.*, 2013) and *f*O₂ at Ni-NiO. Speciation for the gas compositions taken from Gaillard *et al.* (2012) was recalculated for our model conditions.

Fluxing the CO₂-rich gas through H₂O-dominated vapour at 100 and 10 bar reduced Cu solubility by a factor of 50 and 100, respectively (Table 1). Decreasing the temperature to 650 °C, where Cu solubility is highest (Migdisov *et al.*, 2013), and reducing the pHCl for the deeply-exsolved vapour tenfold to include the low volatility of Cl at high pressure (Spilliaert *et al.*, 2006a), had an even greater effect. Copper solubility at 100 bar dropped by four orders of magnitude (725 to 0.08 ppb). In essence, CO₂ reduces the transporting capacity of the vapour to almost nothing, and Cu is deposited or reabsorbed by the melt. Per bar of pressure change, the drop in Cu solubility is 2.9 bar⁻¹ for the 100 to 10 bar change in *P*_{total} at 650 °C, whereas it is 2.9 bar⁻¹ and 82 bar⁻¹ for Δ*p*H₂O at 100 and 10 bar *P*_{total}, respectively (Table 1). When the accompanying reduction in pHCl is taken into account, CO₂-fluxing is 100 to 600 times more effective in lowering Cu solubility per bar than decompression.

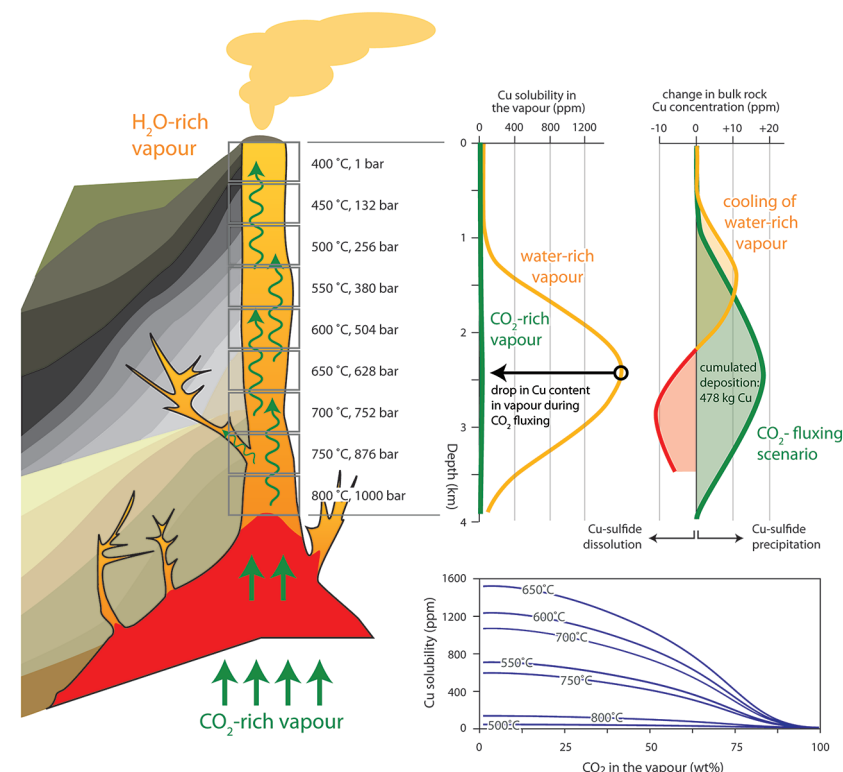


Figure 1 Impact of CO₂-fluxing on Cu solubility in a volcanic conduit filled with vapour. Fluxing deep-sourced CO₂-rich vapour through shallower, water-dominated vapour reduces Cu solubility as the water partial pressure is reduced. Cu contents are significant for the water-dominated vapour. Assuming upward flow, Cu is dissolved from wall rocks to 2.2 km, and subsequently deposited. In contrast, contents in the CO₂-rich vapour are negligible. Therefore, a single pulse of CO₂-rich vapour will deposit essentially all Cu in the water-vapour, with deposition at all depths and all temperatures.

Collins *et al.* (2009) report that melt inclusions from Etna volcano record an approximately twofold enrichment in Cu content, which was attributed to CO₂-fluxing, with gas CO₂ content increasing from 70 to 98 mole %. Unfortunately, the stability constants for the hydrated Cu-chloride species of Migdisov *et al.* (2013) cannot be extrapolated to the 1140 °C reported for these inclusions, which precludes quantitative modelling of this system. To a first approximation, a 270 times decrease in Cu solubility is predicted from the change in pH₂O, for a *P*_{total} of 1000 bar and fayalite-magnetite-quartz buffered *f*O₂. The Etna melt is unlikely to be saturated in chalcopyrite, and this drop therefore represents a maximum concentration change. Nonetheless, it shows that CO₂-fluxing



introduces a sharp reduction in the Cu transporting capability of the gas that can indeed explain the observed correlation between fluxing and Cu contents in Etna melt inclusions.

Table 1 Predicted Cu solubility in vapours of varying $p\text{H}_2\text{O}$ and $p\text{HCl}$ with $f\text{O}_2$ and Cu buffered by NiO-Ni and $\text{CuFeS}_2\text{-FeS}_2$, respectively.

	Vapour	T (°C)	Pressure (bar)			Cu (ppb)	pair	Cu reduction factor	
			P_{total}	$p\text{H}_2\text{O}$	$p\text{HCl}$			absolute	per bar
1	H ₂ O-rich	800	100	24.42	0.5	1.2			
2	CO ₂ -rich	800	100	5.76	0.5	0.02	1 - 2	53	2.9
3	CO ₂ -rich	800	100	5.76	0.05	0.0002	1 - 3	5232	280
4	H ₂ O-rich	800	10	1.41	0.5	0.004			
5	CO ₂ -rich	800	10	0.21	0.5	0.0001	4 - 5	99	82
6	CO ₂ -rich	800	10	0.21	0.05	0.0000	4 - 6	9706	8104
7	H ₂ O-rich	650	100	23.54	0.5	724			
8	CO ₂ -rich	650	100	5.72	0.5	8	7 - 8	91	5.1
9	CO ₂ -rich	650	100	5.72	0.05	0.08	7 - 9	8957	503
10	H ₂ O-rich	650	10	0.81	0.5	3.1			
11	CO ₂ -rich	650	10	0.1	0.5	0.02	10 - 11	148	208
12	CO ₂ -rich	650	10	0.1	0.05	0.0002	10 - 12	14566	20515
	H ₂ O-rich	800	100 - 10		0.5		1 - 4	263	2.9
	H ₂ O-rich	650	100 - 10		0.5		7 - 10	237	2.6

In our simple model, re-establishing a water-rich vapour composition following CO₂-fluxing re-solvates the Cu, and the mechanism is fully reversible. However, kinetic barriers, collapse of a bubble foam as a result of CO₂-fluxing, or choking of vapour pathways by fluxing-induced mineral deposition may preserve these deposits. Moreover, deposition of these elements on conduit walls will lead to their diffusion into the host rock or melt, as a local concentration gradient develops. Transient CO₂-fluxing should thus be best preserved by the fastest diffusing elements, *e.g.*, Li. Melt inclusions with elevated Li content and derived from a magma ponding horizon affected by CO₂-fluxing have indeed been observed (*e.g.*, Berlo *et al.*, 2004; Blundy *et al.*, 2010). However, the lack of stability constants for hydrated Li species in vapour prevents us from evaluating whether CO₂-fluxing is capable of inducing a sufficient drop in Li solubility to generate the observed enrichments.

Metal Enrichment by CO₂-Fluxing

Magmatic-hydrothermal systems can be vertically extensive (*e.g.*, Hedenquist and Lowenstern, 1994). To better represent these, we added a pressure-temperature

gradient (Fig. 1). We assumed that the host rock had reacted to an equilibrium alteration assemblage prior to CO₂-fluxing and therefore did not participate in the reactions. The initial, H₂O-dominated vapour ($X\text{CO}_2 = 0.04$) was Cu-saturated by equilibrating with chalcopyrite, and Cu solubility was tracked along the conduit length. Subsequently, the conduit was fluxed with CO₂-rich vapour ($X\text{CO}_2 = 0.91$) as in the simplified model above. In natural systems, Cu concentrations are unlikely to be at Cu-phase saturation throughout the system and throughout their lifespan (Landtwing *et al.*, 2005), and these calculations thus provide maximum estimates. However, this is also true for other depositional mechanisms, and saturation therefore provides an appropriate benchmark for comparison.

Copper solubility in the water-rich vapour reaches a maximum of 1575 ppm at 650 °C, resulting from the hydrated Cu-chloride species being most stable at this temperature (Migdisov *et al.*, 2013; Fig. 1). In contrast, only 0.2 ppm Cu dissolves in the CO₂-rich vapour at these conditions. Copper solubility decreases with increasing $X\text{CO}_2$ for all temperatures (Fig. 1). Any vapour passing through the conduit will dissolve Cu at temperatures up to 650 °C, and only precipitate it after cooling below this temperature (Fig. 1). In contrast, CO₂-fluxing will result in Cu deposition at *any* temperature, because of the drastic reduction in solubility. In addition, the total amount of Cu deposited in a fluxing scenario is higher than by simple cooling, because of the greater overall reduction in solubility.

Given that water is a more abundant volatile than CO₂, permeable gas networks such as bubble foams in magma and interconnected fracture networks will develop dominantly during release of water-rich fluid. However, once established, such networks allow volumetrically minor CO₂-rich gases to flux through. CO₂ is not consumed by fluxing-induced metal deposition, and a single pulse of CO₂-rich gas can therefore lead to deposition of a significant mass of metal. Using the values calculated in the model above, a single pulse of CO₂-rich vapour would deposit 478 kg of Cu along this 4 km long conduit for a 1 m² conduit cross-section. Assuming a host-rock percolation threshold of 15 vol %, this single pulse would enrich the bulk host rock in Cu by 8 ppm; at 650 °C the maximum pervasive enrichment would be 20 ppm. Depositing the Cu in veins, rather than pervasively, leads to locally higher concentrations, *e.g.*, if these account for 5 % of rock volume, their Cu content peaks at 400 ppm. Although still small, this is for a single batch of fluid, and a single CO₂-pulse, whereas many ore-forming systems are characterised by large fluid volumes in extensive hydrothermal circulation systems (*e.g.*, Sillitoe, 2010).

Enrichment of a fracture network to wt. %-level Cu concentrations, *i.e.* economic levels, necessitates involvement of a water-rich vapour that transports Cu. Metal solubilities in CO₂-rich vapour are negligible, preventing it from acting as a metal carrier, and its role is restricted to providing a highly efficient depositional mechanism. To explore a system where water- and CO₂-rich vapours interact, we limited fluxing to 5 vol. % of the conduit network (Fig. 2a). After each CO₂-pulse, H₂O-rich vapour re-establishes itself in the fluxed part of the fracture network and mixes with the H₂O-rich vapour in the 95 vol. % of the



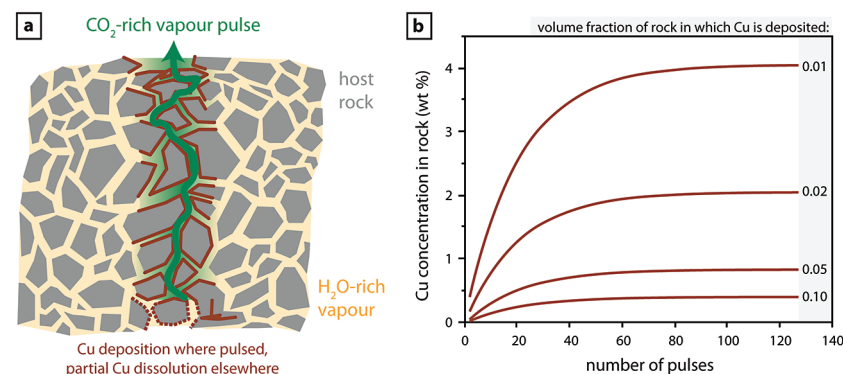


Figure 2 Progressive Cu enrichment in a fracture network intermittently pulsed with CO₂-rich vapour in its centre. (a) Schematic section showing Cu deposition on fracture walls followed by partial re-dissolution after each pulse, except for fractures sealed by precipitation. (b) Progressive enrichment of Cu assuming partial Cu re-dissolution, and fluxing of 5 vol. % of the fracture network. Cu is sourced from the 95 vol. % of the network filled with water-rich vapour.

fracture network. Repeatedly fluxing this 5 vol. % section leads to a rapid increase in Cu content (Fig. 2b). Effectively, this redistributes Cu from the full system and concentrates it in the CO₂-fluxed part. We included a re-dissolution fraction of 5 wt. % of total Cu in each calculation step, which can be interpreted as slow kinetics of re-dissolution, or short lifespans for individual fractures. Choosing a higher fraction necessitates more CO₂-pulses to reach these Cu concentrations, but otherwise does not affect the model. Cu contents in the fluxed part of the fracture network readily reach wt. % concentrations (Fig. 2b).

Conclusions

We propose that CO₂-fluxing is a highly efficient metal deposition mechanism that rivals established ore-depositing mechanisms. It can concentrate Cu to levels that are economic to mine in porphyry-Cu ore deposits. However, porphyry-Cu systems provide a benchmark only, and we do not advocate their formation by CO₂-fluxing, because the combination of invoked geological conditions is unlikely to be present in these systems. Rather, CO₂-fluxing has the potential to control metal contents in gas-fluxed magmas and on a local scale in associated hydrothermal systems. In the models presented here, metal deposition results from lowering water partial pressure and this can be brought about not only by fluxing with CO₂, but also by fluxing with other gases (e.g., N₂). It is moreover not restricted to vapours, but will also impact solubility for hydrated species in aqueous solutions (e.g., Akinfiev and Diamond, 2009), albeit less drastically.

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1617

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CO₂-fluxing collapses metal mobility in magmatic vapour

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Supplementary Information

The Supplementary Information includes:

- Details on Calculations and Methodology
- Table S-1
- Supplementary Information References

Details on Calculations and Methodology

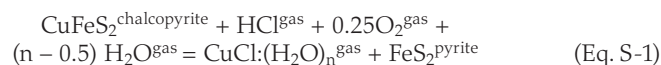
Thermodynamic calculations

The solubility of Cu in the CO₂-H₂O(-HCl) vapours was calculated from thermodynamic stability constants for the relevant vapour species and the H₂O-CO₂ medium at the temperatures and pressures of the respective simulations. To set model boundary conditions for the oxygen fugacity and Cu activity, each vapour was equilibrated with a mineral assemblage consisting of chalcopyrite, pyrite, Ni and NiO. Chalcopyrite is the most common Cu-mineral in nature, and likely controls the solubility of copper in a wide variety of environments. Its presence, together with that of pyrite, saturates the vapour in Cu at a level representative for many Cu mineralisations. Ni and NiO buffer the oxygen fugacities of the system, but do not partake in the speciation reactions as no other Ni-species bar Ni_(s) and NiO_(s) were allowed to form. Calculations for Etna volcano were performed with oxygen fugacity fixed by the assemblage fayalite-magnetite-quartz.

Copper saturation of an HCl-bearing vapour with Cu-bearing species is controlled by the following reactions (Migdisov *et al.*, 2013):

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The Cu solubility calculations thus involved the following species: CuCl^{gas} , $\text{Cu}_3\text{Cl}_3^{\text{gas}}$, $\text{CuCl}:(\text{H}_2\text{O})_n^{\text{gas}}$, $\text{CuCl}:\text{HCl}:(\text{H}_2\text{O})_{2.5}^{\text{gas}}$, HCl^{gas} , O_2^{gas} , $\text{H}_2\text{O}^{\text{gas}}$, and CO_2^{gas} . Considering that data on the stability of the hydrated gaseous Fe-bearing chlorides as well as the hydrated Cu-(H)_xS_y species are not available, these species were not accounted for in the modelling. Reduced sulphur species are known to solvate Cu in aqueous vapour (*e.g.*, Simon *et al.*, 2006; Zajacz *et al.*, 2011), and excluding these from the present calculations will thus underestimate the solubility of Cu. Fugacity and partial pressures of pure water were calculated using the equation of state reported in Kestin *et al.* (1984); gaseous mixtures as well as the properties of pure HCl^{gas} , O_2^{gas} , and CO_2^{gas} were modelled using the PRSV equation of state (Stryjek and Vera, 1986); hydrated copper chlorides were assumed to obey the Ideal Gas Law. The calculations were performed using the HCh software package for geochemical equilibrium modelling (Shvarov and Bastrakov, 1999). Thermodynamic properties required for these calculations were taken from Migdisov *et al.* (2013) for the Cu/Cl species, and from Robie and Hemingway (1995) and Holland and Powell (1998) for chalcopryrite, pyrite, Ni, NiO, magnetite, fayalite, quartz, HCl^{gas} , O_2^{gas} , and CO_2^{gas} .

Single CO₂-pulse model

In the simplest scenario, we model a single pulse of CO₂-rich vapour passing through a, for simplicity, static water-dominated vapour at 800 °C (in principal only relative movement of the CO₂ vapour is required and both could be moving up the conduit in absolute terms). The CO₂ vapour pulse is assumed to diffuse into the water-rich vapour and change the vapour's composition to that of the CO₂-dominated vapour, *i.e.* changing the medium without a change in total pressure. In natural systems, introduction of a CO₂-rich vapour may lead to a rise in P_{total} , which will reduce the impact of the decrease in $p\text{H}_2\text{O}$. However, given that the effect of a change in $p\text{H}_2\text{O}$ exceeds that resulting from a change in P_{total} per bar of change (Table 1), it is unlikely able to compensate. Cu solubility was calculated at 10 and 100 bar in both water- and a CO₂-dominated vapour. The compositions of the water-dominated vapour at 10 and 100 bar are those in equilibrium with mafic magma at these pressures, as taken from Gaillard *et al.* (2012). The CO₂-dominated vapour pulse is the composition of the vapour in equilibrium with this same mafic magma at 1000 bar from Gaillard *et al.* (2012), with its speciation and species fugacities recalculated for 10 or 100 bar using the thermodynamic data and models detailed above. In the first set of calculations, $p\text{HCl}$ was kept constant at 0.005 to isolate the effect of CO₂ on solubility. However, the deep-degassed CO₂-rich vapour pulse will have a lower HCl content, because Cl-solubility in the melt is strongly pressure dependent (Spilliaert *et al.*, 2006). To

show the combined impact of lowering $p\text{H}_2\text{O}$ and $p\text{HCl}$, we reduced the $p\text{HCl}$ by an arbitrary factor of 10. The model of Witham *et al.* (2012) predicts a more than tenfold decrease for a typical basalt when comparing the exsolved gas at 1000 bar to that at 10 bar, showing that this is a reasonable reduction. Lowering the $p\text{HCl}$ further reduces the Cu solubility (Tables 1 and S-1).

Table S-1 Gas compositions used in the calculations and calculated Cu solubility.

Conditions	CO ₂ -rich vapour pulse			Receiving vapour	
T (°C)	800	800	800	800	800
P (bar)	1000	100*	10*	100	10
Input gas composition in bar					
pCO ₂	1116	90	8.7	62	2.9
pCO	83	6.1	0.66	0.4	0.02
pH ₂ O	8.7	1.41	0.21	24	5.8
pH ₂ S	48	3.93	0.31	12	0.99
pH ₂	0.71	0.1	0.02	0.17	0.04
pS ₂	1	0.33	0.07	1.1	0.13
pSO ₂	0.004	0.003	0.001	0.59	0.18
Calculated Cu solubility in ppb					
Cu	-	0.022	4.6 10 ⁻⁵	1.18	4.5 10 ⁻³

* These CO₂-rich vapours represent the 1000 bar vapour with partial pressures recalculated to equilibrium values at 100 and 10 bar using the thermodynamic data listed above.

Our calculations do not consider all Cu-species that have been proposed to control Cu solubility in vapour for lack of the thermodynamic data to model these. Hydrated Cu-(H)_xS_y species, in particular, are regarded as important carriers of Cu in vapour (*e.g.*, Simon *et al.*, 2006; Zajacz *et al.*, 2011). The impact of CO₂-fluxing on the stability of such species cannot be assessed quantitatively, but qualitatively. Addition of CO₂ will result in dilution of the constituent elements of these species, thereby reducing their partial pressures, *e.g.*, $p\text{H}_2\text{S}$, which will lower the stability of these species and, hence, the solubility of Cu. Including additional Cu-species thus changes the absolute value of the Cu solubility, but these species are similarly affected by CO₂-fluxing, and a strong reduction in Cu content in the vapour will hence still ensue.

Conduit model

To evaluate the impact of changes in metal solubility resulting from CO₂ fluxing in a geological environment, we modelled a vapour filled magmatic-hydrothermal conduit or fracture network (Fig. 1). Temperature decreased linearly in this conduit from 800 to 400 °C and the system was subjected to a lithostatic pressure gradient using a wall-rock density of 2700 kgm⁻³ (*i.e.* dacite) from 1000 to



1 bar. Solubilities were calculated for a typical, water-dominated arc-volcanic gas emitted from an andesitic-dacitic volcanic system ($X_{H_2O} = 0.953$; $X_{CO_2} = 0.035$; $X_{CO} = 2 \cdot 10^{-8}$; $X_{H_2S} = 6.9 \cdot 10^{-3}$; $X_{SO_2} = 4.9 \cdot 10^{-3}$; $X_{H_2} = 2 \cdot 10^{-7}$; $X_{HCl} = 1.13 \cdot 10^{-3}$), progressively fluxed by the CO_2 -rich vapour listed in Table S-1. Major and trace element vapour speciation was recalculated for each set of P - T conditions using the thermodynamic data and models listed above. This system mimics a dacite-hosted magmatic-hydrothermal system fluxed by CO_2 -rich vapours released from a deeper mafic magma. The system is assumed to be in equilibrium and no exchange between host rock and vapour takes place except for that involving Cu solubility (see above), *i.e.* the host rock has been altered to a mature secondary silicate mineral paragenesis in equilibrium with the vapour and therefore acts as a passive boundary. There is no vertical movement of the water-dominated vapour through the conduit.

To calculate the amount of Cu deposited by fluxing, we integrated the area under the solubility curves for the most water-rich and most CO_2 -rich vapours to arrive at the total mass of Cu in the conduit for each vapour, the difference of which represents the mass deposited. An interconnected fracture network reaches permeability at ~15 vol. % and we took this number as the fraction of the conduit or fracture network occupied by vapour (fluxing requires a permeable network). The mass of depositing Cu was hence distributed over 85 vol. % of dacite at a density of 2700 kgm^{-3} to determine the increase in Cu content in the host dacite for a single pulse of CO_2 -rich vapour assuming pervasive deposition of Cu and a cylindrical conduit. Deposition of Cu per unit conduit length was similarly calculated by splitting the conduit into 9 sections at 50°C spacing (Fig. 1) and integrating the solubility curve area for each section.

Pulsed conduit model

Vapours rich in CO_2 have negligible transporting capacity for Cu. This means that fluxing by such vapours does not add metal to the system and only represents a highly efficient depositional mechanism. To form a mineralisation thus requires involvement of a water-dominated vapour to act as the metal-carrying medium. In our final model, we represent such a system by assuming that only 5 % of the conduit or fracture network is fluxed by CO_2 -rich vapour for any given pulse, and pulses are repeated. Multiple pulses of vapour with varying $X(CO_2)$ are known from a number of volcanoes. Etna volcano, in particular, has displayed rapid and persistent fluctuations in $X(CO_2)$ on timescales from minutes to weeks (Allard *et al.*, 2005; Aiuppa *et al.*, 2007). The compositions of the water-rich and CO_2 -rich vapours and, hence, their Cu solubility, are as in the preceding model. As above, the fracture network has a 15 vol. % permeability and is hosted by dacite with a 2700 kgm^{-3} density.

Each model step consists of:

1. A pulse of CO_2 -rich vapour passing through 5 vol. % of the fracture network filled with water-dominated vapour saturated in chalcopyrite thereby leading to Cu deposition. This step corresponds to the conduit model described in the preceding section.
2. Subsequently, the vapour in this 5 vol. % section is mixed with the water-rich vapour remaining in the rest of the fracture network, and 5 wt. % of the chalcopyrite deposited is allowed to re-dissolve into this vapour as long as this does not exceed Cu solubility (alternatively, Cu re-dissolves up to this solubility limit). This step represents the re-establishment of the water vapour, after the CO_2 -pulse has passed, by an influx of water-rich vapour from the rest of the fracture network. The 5 wt. % re-dissolution limit is arbitrary and was set to simulate kinetic hindrance of chalcopyrite re-dissolution and sealing off of fractures by mineral precipitation during the deposition event. Such sealed sections will no longer participate and are a well-established feature of many mineralisations, including porphyry Cu deposits as evidenced by multi-stage and crosscutting vein relationships (Sillitoe, 2010).

Pulses were subsequently repeated, leading to a progressive enrichment of Cu in the fluxed part of the fracture network. This Cu is sourced from the 95 vol. % of the fracture network not being fluxed, and this model thus represents a redistribution of Cu with the water-rich vapour acting as the transporting agent, and local enrichment as a result of Cu deposition by CO_2 -fluxing. Enrichment slows with pulse number because the relative contribution from the water vapour mixing back in decreases over time compared to the residual Cu resulting from incomplete re-dissolution. Increasing the re-dissolution fraction slows the build-up of Cu, but it does reach the same concentrations (except when the re-dissolution fraction = 1, because in this case all Cu is re-dissolved and thus reaches its solubility limit and no Cu is hence redistributed into the fluxed part of the fracture network).

Deposition of metals in many ore-deposits, for example Cu-porphyry systems, is not pervasive, but concentrated in discrete veins (Sillitoe, 2010). To simulate this, a "volume fraction of receiving wall rock" was introduced into the model. A value of 1 represents complete pervasive deposition, whereas lower values represent progressive concentration of Cu on fracture walls (Fig. 2a), *i.e.* forming chalcopyrite veins. From integration of the solubility curve area following the approach described above for the conduit model we calculate the concentrations of Cu in these fracture walls for a number of volume fractions (Fig. 2b) and show that these concentrations correspond to levels found in economically viable Cu deposits for volume fractions of less than ~5 %. This would represent a mineralised system where chalcopyrite veins make up less than 5 vol. % of the total hydrothermal fracture network.



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